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Sol–gel preparation of well-adhered films and long range ordered inverse opal films of $BaTiO_3$ and $Bi_2Ti_2O_7$

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ABSTRACT

Barium and bismuth titanate thin films and well-ordered inverse opal films are produced by dip coating from sols containing titanium alkoxides with acetic acid, acetylacetone, methoxyethanol and water. The inverse opal preparations used crosslinked polystyrene opal templates. Heat treatment in air produced tetragonal $BaTiO_3$ or mixtures of the hexagonal and tetragonal phases, or phase pure $Bi_2Ti_2O_7$. Good quality films were obtained with a thickness of 5 μm from a single dipping, and the thickness could be increased by dipping multiple times. Inverse opals were well ordered and exhibited opalescence and photonic stop band effects.

1. Introduction

Electroceramic materials are often ternary or higher oxides containing transition metals in combination with larger cations. $BaTiO_3$ is one of the most important and best established of these, with ferroelectric and piezoelectric properties that have been utilised in capacitors, microphones and other devices [1]. $Bi_2Ti_2O_7$ is less well studied and more difficult to utilise in devices due to a poor thermal stability [2], but is a linear dielectric with high permittivity values at room temperature and exhibits a temperature and frequency-dependent dielectric relaxation [3]. It has no ferroelectric behavior since, although large displacements are present in the Bi and O' sites with correlations between them, these correlations exhibit a high degree of frustration due to the tetrahedral network arrangement of these sites within the Bi_2O' sublattice of the pyrochlore structure [4].

Electroceramics are often prepared as powders and then processed into the required form with a high temperature sintering process. Both $BaTiO_3$ [5–7] and $Bi_2Ti_2O_7$ [8,9] have also been produced as films using vapor phase deposition techniques, which is an effective option for making thin, dense, flat films. Sol–gel routes, however, have advantages in scalability, adaptability to a variety of substrates and access to a variety of porous architectures via deposition into the spaces of various hard or soft templates [10]. Sol–gel recipes for such ternary oxides need to take account of the high hydrolytic sensitivity of titanium alkoxides, so often use strongly coordinating solvents such as acetic acid and reaction moderators such as acetylacetone to control this reactivity [10]. Controlled water contents also contribute to formation of stable sol compositions. In this work we combine these control measures to make good quality films of $BaTiO_3$ and $Bi_2Ti_2O_7$. The prior art in these areas is covered in detail in the relevant sections of the paper.

Inverse opal structures can be produced by filling the spaces in templates formed from close-packed arrays of spheres. They have been produced in a wide range of materials due to potential applications as photonic band gap materials [11], battery electrodes [12], gas sensors [13], catalysts [14–16], membranes [17], and biomaterials [18]. We previously used heavily cross-linked polystyrene spheres with good solvent resistant properties to produce inverse opal films in metal nitrides [19,20]. Herein we show that these templates, combined with the same sol formulations used to produce this films, are effective in production of highly ordered inverse opal films of $BaTiO_3$ and $Bi_2Ti_2O_7$.

2. Materials and methods

Variations in the $BaTiO_3$ precursor sol composition are discussed in the results and discussion, but typically barium acetate (2.5 g, Sigma–Aldrich, 99%) was dissolved in glacial acetic acid (15 mL, Fisher) at 60 °C followed by addition of deionised

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water (1.0 mL), the solution was stirred for a further 10 min then allowed to cool to room temperature in a sealed bottle. Titanium isopropoxide (3 mL, Aldrich, 97%) was dissolved in anhydrous 2-methoxyethanol (15 mL, Sigma–Aldrich, 99.8%) and acetylacetone (1.46 mL, Sigma–Aldrich, >99%) was added as a moderator to control the hydrolysis rate of the titanium isopropoxide. The barium acetate solution was added drop-wise to the titanium isopropoxide solution with stirring over a period of ~1 h and the resultant translucent and light yellow sol was aged in a sealed bottle at room temperature for 24 h.

In a typical $Bi_2Ti_2O_7$ sol preparation, $Bi(NO_3)_3{\cdot}5H_2O$ (6.8869 g, Aldrich, 99.99 %) was dissolved in glacial acetic acid (15 mL) at 50 °C and the solution was allowed to cool to room temperature in a sealed glass bottle. Titanium n-butoxide (5 mL, Aldrich, 97%) was dissolved in a mixture of 2-methoxyethanol (15 mL) and acetylacetone (1.46 mL) and stirred for 5 min. The bismuth nitrate solution was added drop wise to the titanium butoxide solution over ~1 h and the resultant translucent, dark yellow sol was aged in a sealed bottle at room temperature for 24 h.

Glass microscope slides (Fisher) or (100) silicon wafers (IDB Technologies Ltd.) were cut to 10 × 20 mm and used as substrates for $Bi_2Ti_2O_7$ or $BaTiO_3$ (respectively) film depositions. The substrates were cleaned in piranha etch (3:1H_2SO_4:H_2O_2, [21]) for ~3 h to completely remove organic contaminants (*note this can produce explosive mixtures if incorrectly prepared*), rinsed with water then ethanol, and blown dry with nitrogen. Using a Nima Technology D1L dip-coater a 10 × 10 mm region of the substrate was immersed into the sol for 5 s and then withdrawn at a rate of 65 mm min^{-1}. The drop of excess sol at the bottom of the substrate was removed with tissue and then films were placed horizontally on a petri dish to age/dry in air for ~30 min. The films were annealed in air by placing into a pre-heated furnace at various temperatures for 40 min.

Inverse opal film preparations used close packed sphere templates produced from 500 nm DVB-crosslinked, amidine capped polystyrene spheres (Invitrogen) on one half of 20 × 20 × 1 mm fused silica tiles as described previously [19]. The template was dipped into the $BaTiO_3$ or $Bi_2Ti_2O_7$ precursor sol and withdrawn at 75 mm min^{-1}, left to dry in air in the vertical position for 30 min, and then the process was repeated once ($Bi_2Ti_2O_7$) or twice ($BaTiO_3$). The films were heated at 5 °C min^{-1} to various temperatures to remove the template and anneal the titanate materials, the temperature was maintained for 30 min and samples were allowed to cool in the furnace.

Films and inverse opals were imaged using a Philips XL30-ESEM in environmental mode to avoid sample charging. Energy dispersive X-ray (EDX) spectroscopy used a ThermoFisher Ultradry probe. Grazing incidence X-ray diffraction studies used a Rigaku Smartlab Thin Film diffractometer with Cu-Kα radiation, a 0.1 mm parallel beam, a 1° incident angle and a DTex 250 1D detector. Rietveld fitting used the GSAS package [22,23] and structural models from ICSD [24]. Crystallite sizes were extracted from the GSAS particle size broadening term as described in the GSAS manual [25].

3. Results and discussion

$BaTiO_3$ and $Bi_2Ti_2O_7$ films and inverse opals were produced from sols in acetic acid/methoxyethanol mixtures. Films with a thickness of ~5 μm were produced by dip coating once and firing the dried films, and multiple dip/dry cycles could be used to build up larger thicknesses. Inverse opal production used close-packed polymer sphere films as described previously [19] and multiple dip coating cycles to completely fill the interlayer space.

3.1. $BaTiO_3$ films

Existing sol–gel routes to $BaTiO_3$ films typically employ Ti(O^iPr)$_4$ and barium acetate [26–29], hydroxide [30], isopropoxide [31] or ethylhexanoate [32] in acetic acid [29], alcohols [30,31] or mixtures of acetic acid and alcohols [26–28,32]. A reaction moderator such as acetylacetone [32], diethanolamine [31] or ethylene glycol [30] may be added to control the hydrolysis of the Ti(O^iPr)$_4$, although this functionality can also be achieved via acetate groups from the acetic acid or by using methoxyethanol in the solvent mixture [27,28], which can displace isopropoxide groups from the titanium and block additional coordination sites via coordination of the ether group. A final variation is that some researchers have added water to the mixture in order to gain better control of its concentration rather than relying on moisture from the reagents and the atmosphere as a source of this component, which is critical in all cases for the hydrolysis of the precursors.

It is not typical to combine all of the controls described above in a single process. In most cases very thin films, of the order of tens of nm per coating, are produced and procedures rely on multiple coating/drying cycles to build film thickness. An exception to this is the work of Yuk and Troczynski who produced heavily cracked 7.5 μm thick coatings from acetic acid sols with no added alcohol [29]. The ability to produce good quality thicker films in a single coating is useful because it would then be possible to dilute sols with extra alcohol to control the film thickness over a wide range. Hence in this work water was added to sols in order to increase the concentration of hydrolysed species and enhance condensation during solvent evaporation. Stabilisation of these sols required a strongly coordinating environment and sols containing acetate and acetylacetone diluted with methoxyethanol were found to be stable and clear. Kamalasanan et al. previously applied a similar approach, but with methanol as the solvent [32]. They did produce thicker films by reducing the methanol content of the sols, but suffered from poor adhesion in the thicker films.

$BaTiO_3$ films were produced using barium acetate and titanium isopropoxide with an acetic acid/methoxyethanol solvent mixture, acetylacetone reaction moderator and controlled water content. Initially a range of sol compositions was investigated in which the water content was varied. Use of only a small trace of water (0.007 mL) resulted in films that had roughly 100 μm circular regions that had delaminated and that, after firing, contained a mixture of $BaTiO_3$ and $BaTi_2O_5$. Increasing the water content to 0.7 mL led to a significant improvement in film quality, though with significant numbers of pinholes, and firing at 750 °C produced cubic $BaTiO_3$ with a small amount of hexagonal $BaTiO_3$. With 1 mL water the films were smooth and well adhered. These descriptions are based on the central regions of the films, and regions around the edges often had some degree of cracking and occasionally pinholes. Any increase in the acetylacetone concentration beyond that described in the experimental section was found to lead to an increase in cracking and pinhole formation across the entire film.

Shortening the sol aging time resulted in changes to the film composition and phase content. A film produced from an unaged sol and heated at 900 °C for 40 min contained mainly $BaTi_2O_5$ with some hexagonal $BaTiO_3$ (Fig. 1). Surprisingly EDX showed this film also to be barium deficient, suggesting that the sol itself is inhomogeneous at this point (the bulk content of the sol has a 1:1 Ba:Ti ratio). A 3 h sol aging time resulted in a decrease in the intensity of the $BaTi_2O_5$ peaks in a film heated under the same conditions, and after 9 or 24 h sol aging the $BaTi_2O_5$ peaks were not observed, although peaks due to the $Ba_2TiOSi_2O_7$ fresnoite phase were observed. This phase has previously been shown to grow at the $BaTiO_3$/Si interface when films are heated above 730 °C [33]. The film from the sol aged for 24 h had a Ba:Ti ratio of 1:1.0. This importance of sol aging time suggests that a certain level of